Extraction of vanadium from Philippine iron ores

Karl Justine V. Abang, Carina V. Pecson

Metallurgical Technology Division, Mines and Geosciences Bureau, North Avenue, Diliman, Quezon City
kjvabang@gmail.com, carina_pecson@yahoo.com

ABSTRACT

Vanadium is a transition metal primarily used in the production of steels, as well as a chemical catalyst and alloying element. The Philippines, which is rich in iron resources, has a potential to use its iron ores for vanadium production. The demand for vanadium is expected to increase in the upcoming years due to its commercialization for large-scale energy storage applications. The study examines the feasibility of vanadium extraction from titanomagnetite ores in the country. Iron ores from Camarines Norte, Leyte, and Zamboanga were extracted via direct leaching method. Calcium fluoride addition (3-5 wt.%), solid-liquid (S/L) ratio (2.5-3.5 ml/g), and sulfuric acid concentration (4-5 M) were optimized using Response Surface Methodology (RSM) based on a three-factor, three-level Box Behnken design. Results of the statistical analyses suggest that the optimum leaching parameters are 4.02 wt.%, 2.74, and 4.73 M calcium fluoride addition, S/L ratio, and sulfuric acid concentration, respectively. Under these conditions, vanadium recovery of 88.67% is achieved. The results of the direct leaching test validates the efficiency of the direct leaching method on vanadium extraction employed to the iron ores of the country.

Keywords—Vanadium extraction, direct leaching, optimization, response surface methodology, Box-Behnken Design

---

1. Introduction

Vanadium (V) is a transition metal widely used in the production of high-quality ferrous and non-ferrous alloys, and chemical catalysts [1] . Eighty-five percent (85%) of vanadium globally is used in the steel industry, where 0.05-0.2% V is utilized in the production of High-Strength Low-Alloy (HSLA) steels [1,2]. Vanadium is primarily known to improve the strength of titanium and vanadium-titanium alloys, which are used in the production of aircraft. Heat exchangers in nuclear reactors also utilize V-Cr-Ti alloys which are durable at high temperatures, and corrosion resistant. Vanadium compounds are also used as catalysts in the chemical industry. Oxides of vanadium are known to speed up the chemical reaction in the formation of sulfuric acid.

Vanadium occurs in nature as part of the following minerals: carnotite, mica, vanadinite, mottramite, and patronite [3]. The common oxidation states for vanadium are +2, +3. +4, and +5. In particular, the trivalent ion $V3+$, has an octahedral radius of 0.061 nm, which is nearly identical to the radius of a $Fe3+$ ion (0.063 nm). As a result, vanadium is mostly associated with iron-rich minerals, such as magnetite, pyroxene, amphibole, and biotite. It also replaces aluminum (0.056 nm) in case of ferric minerals containing magnesium. It is also abundant in mafic igneous rocks, while rocks of ultramafic and intermediate composition contain vanadium and lesser amounts [3]. Vanadium is also present in organic shales, with average concentrations of 130-205 ppm.

The extraction of vanadium from titano-magnetite ores are divided into two major categories: direct extraction (from ores), and indirect extraction from slag after ironmaking and steelmaking [4]. The former involves roasting the ore with NaCl or Na2CO3 at above 1000˚C followed by water leaching. Indirect extraction, on the other hand, is the main method in vanadium pentoxide production, which is comprised by the following steps: roasting with Na_2CO_3, water leaching, precipitation and purification [4].

However, an increase in the demand for vanadium is expected to happen in the upcoming years, primarily due to the prospect of vanadium as a main material for energy storage applications. Vanadium has been widely used in the production of redox flow batteries – a new technology that allows the charge and discharge of energy simultaneously [1]. In particular, the use of vanadium redox flow batteries (VRB's) is a novel method in the stabilization of high amounts of energy. This is used in applications such as energy storage in wind generation facilities.

The Philippines is rich in iron ore, particularly in the form of magnetite. In estimate, around 1.56 billion MT of ore containing 5.7-64,4% magnetite are part of the country's resources [5]. However, majority of the iron ores are subjected to minimal value adding and are directly exported to other countries. Hence, there is still no current production of vanadium in the country. With this in consideration, the study aims to introduce a viable method of vanadium extraction that is both technically and environmentally acceptable – one that will aid in the development of a value-adding activity in the mineral sector. This will enhance the value of iron ores in the country with the generation of new products in the market. In addition, this will also benefit the steel industry as it can be a source of raw concentrates to improve the quality of steel products.

In this work, the feasibility of vanadium extraction using iron ores in the country is investigated. In addition, Direct leaching,

a promising method of vanadium extraction, was employed. Optimization of leaching conditions (calcium fluoride addition, solid-to-liquid ratio, and sulfuric acid concentration), were carried out through response surface methodology (RSM) based on the Box-Behnken Design (BBD). In addition, the effects of these induvial parameters to vanadium recovery were investigated. Vanadium recovery in these conditions were assessed in order to evaluate the feasibility of vanadium extraction from Philippine iron ores via direct leaching method.

2. Methodology

2.1. Materials

The magnetite ore samples were collected from Jose Panganiban, Camarines Norte, Tolosa, Leyte, and Vitali, Zamboanga. After crushing and grinding, the particle size of the samples is -0.074 mm (200 mesh), accounting for 90% passing. The samples were subjected to a dry, low-intensity magnetic separation. Afterwards, the samples were analyzed using X-ray Diffraction (XRD), and Inductive Coupled Spectroscopy (ICP) to determine the mineral and chemical compositions, respectively. The results of the analyses are shown below:

Table 1: Chemical analysis of the raw ore

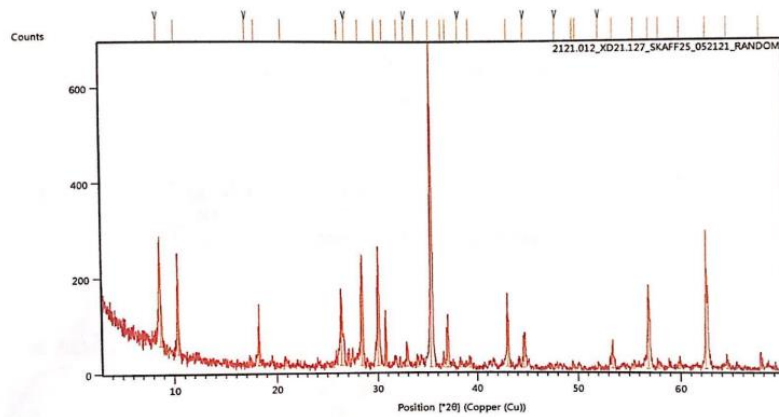| Chemical Composition	TFe	V2O5	TiO2	Al2O3	SiO2	CaO	MgO
Magnetite Ore	49.68	0.532	0.27	3.49	20.33	5.83	3.95

Fig.1. XRD Analysis of the raw ore sample

2.2. Direct leaching method

The titanomagnetite ore samples were crushed to -0.074 mm, accounting for 90% passing. 100 g of ore samples are dissolved in a solution containing 4-5 M sulfuric acid, to produce a leaching setup with S/L (mL/g) ratios of 2.5-3.5. Beforehand, 6-10 g of calcium fluoride were allowed to dissolve in the acid solution. Leaching was performed at a constant time, temperature, and stirring rate of 3 h, 95°C, and 300 rpm, respectively. The leaching residue were filtered and the pregnant solutions were prepared for vanadium analysis. The leaching recovery of vanadium was calculated using the equation below:

$$\alpha = \frac{m-n}{m} \, x \, 100 \tag{1}$$

where α is the vanadium recovery (%) , m is the amount of vanadium in the pregnant solution, and n is the vanadium present in the leaching residue [4].The optimization of the direct leaching process was performed by employing a three level, three-factor Box-Behnken Design

(BBD). The parameters varied in the optimization are calcium fluoride addition (wt.%), S/L ratio (mL/g), and sulfuric acid concentration (M). Low, mid, and high levels were coded as -1, 0, and 1, respectively. The BBD experimental design is shown in Table 2. The statistical relevance of the results were analyzed using the coefficient of determination (R^2), analysis of variance (ANOVA), and response plots. For the latter, Response Surface Methodology (RSM) was applied to fit the experimental data into a second-order polynomial equation:

$$Y_{pred} = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_{ij} + \varepsilon \tag{2}$$

where Y_{pred} represents the response variable, i.e., the vanadium recovery for the direct leaching method, β_0 is the constant coefficient, βi is the ith linear coefficient of the input factor x_i (i = 1-3), β_{ii} is the ith second-order coefficient of the input factor x_i, β_{ij} is the different interaction coefficients between input factors x_i and x_j (j = 1-3, i $\neq$ j), and ε is the error of the model [6].

Table 2
Experimental setup based on the Box-Behnken design with the corresponding actual and predicted vanadium recovery

Runs	Calcium fluoride addition	S/L ratio	Sulfuric acid concentration	Vanadium recovery, experimental (%)	Vanadium recovery, predicted (%)
1	1	-1	0	75.81	76.45
2	1	0	-1	69.31	70.91
3	0	0	0	86	87.81
4	1	1	0	71.01	70.52
5	0	-1	1	86.61	87.72
6	-1	-1	0	75.77	76.26
7	0	1	1	74.91	77.15
8	0	-1	-1	81.3	79.06
9	0	0	0	86.58	87.81
10	-1	0	1	76.33	74.73
11	0	1	-1	81.87	80.76
12	0	0	0	90.84	87.81
13	-1	1	0	73.96	73.32
14	-1	0	-1	74.01	75.76
15	1	0	1	78.72	76.98

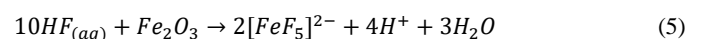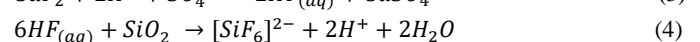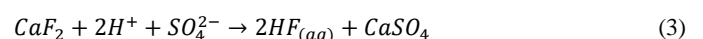# 3. Results and Discussion

3.1. Optimization of direct leaching of vanadium

Table 3
ANOVA results for the second-order polynomial regression

Source	Sum of squares	df	Mean square	F-value	P-value	
Model	531.46	9	59.05	7.58	0.0191	significant
A-Calcium fluoride addition	3.41	1	3.41	0.4373	0.5377	
B-S/L ratio	39.34	1	39.34	5.05	0.0745	
C-Sulfuric acid concentration	12.70	1	12.70	1.63	0.2577	
AB	2.24	1	2.24	0.2869	0.6152	
AC	12.57	1	12.57	1.61	0.2599	
BC	37.64	1	37.64	4.83	0.0793	
A²	378.49	1	378.49	48.59	0.0009	
B²	46.39	1	46.39	5.96	0.0586	
C²	35.25	1	35.25	4.52	0.0867	
Residual	38.95	5	7.79			
Lack of Fit	24.98	3	8.33	1.19	0.4864	not significant
Pure Error	13.97	2	6.98			
Cor Total	570.40	14				

In magnetite, vanadium usually occurs as V^{3+}, which acts substitutional solid in iron. Due to the similarities of octahedral radii of vanadium and iron, which are 0.061 nm and 0.063 nm, respectively, mineral processing is not a feasible method of liberating vanadium from the ore [7]. In addition, V^{3+} is not easily leached by sulfuric acid. Hence, the addition of calcium fluoride is employed to strengthen the leaching process.

Zhu et al. (2016) reported that to achieve 85% vanadium recovery, 8 M sulfuric acid should be used (provided the appropriate leaching parameters). This is indicative of the high acid consumption of the conventional leaching method. In their study, the same vanadium recovery was obtained by adding 5% CaF_2. The reactions that occur with the addition of CaF_2 in the leaching process are as follows:

$$CaF_2 + 2H^+ + SO_4^{2-} \rightarrow 2HF_{(aq)} + CaSO_4 \tag{3}$$

$$6HF_{(aq)} + SiO_2 \rightarrow [SiF_6]^{2-} + 2H^+ + 2H_2O \tag{4}$$

$$10HF_{(aq)} + Fe_2O_3 \rightarrow 2[FeF_5]^{2-} + 4H^+ + 3H_2O \tag{5}$$

In these reactions, the addition of CaF_2 converts sulfuric acid into hydrofluoric acid, a much stronger acid capable of dissolving vanadium into the solution. This is indicated by the decrease in the amount of sulfuric acid to obtain the same vanadium recovery. In addition, the leaching process becomes much more effective due to the formation of $[SiF_6]^{2-}$ and $[FeF_5]^{2-}$ [4].

The direct leaching parameters: calcium fluoride addition, S/L ratio, and sulfuric acid concentration were optimized using response surface methodology (RSM) based on the Box-Behnken Design (BBD). The results of the optimization experiments are shown in Figure 2. After direct leaching, the obtained vanadium recovery ranges from 69.31-90.84%. The highest vanadium recovery is obtained at the following combination of factors: 4 wt.% calcium fluoride, 3 mL/g solution, and 4.5 M sulfuric acid.

The empirical relationship between the vanadium recovery and the independent variables were generated using the BBD. The second-order polynomial equation is shown by:

$$\%recovery_{pred} = 87.81 - 0.6525A - 2.22B + 1.26C - 0.7475AB + 1.77AC - 3.07BC - 10.12A^2 - 3.54B^2 - 3.09C^2 \quad (6)$$

where A, B, and C represent calcium fluoride addition, S/L ratio, and sulfuric acid concentration, respectively. The results of the analysis of variance (ANOVA) is shown in Table 3. ANOVA is used to determine the accuracy of the generated-order polynomial model, as well as the significance of the individual factors and their interactions to the response variable (vanadium recovery). The significance level of each factor and their interactions is depicted by their p-value. If $p < 0.05$, then the factor is considered to be statistically significant; $p > 0.1$ means that the factor is insignificant. Hence, based on the ANOVA table, the effects of B, BC, A^2, B^2, and C^2 are statistically significant. The polynomial model has an F-value of 7.58, This implies that the model has only a 1.91% chance of occurring due to noise or random error [6,8]. Meanwhile, the lack of fit F-value of 1.19 means that the lack-of-fit is not significant with respect to pure error [8,9]. The two F-values suggest that the model can be used as a response predictor for vanadium recovery. Meanwhile, regression analysis indicate an R^2 value of 0.9317, which indicates a good correlation between the experimental and predicted vanadium recovery based on the model. Finally, the signal to noise ratio represents the adequacy precision, and a value greater than 4 is desirable. The model has an adequacy precision of 7.586, indicating the signals in the experimental design are adequate [10].
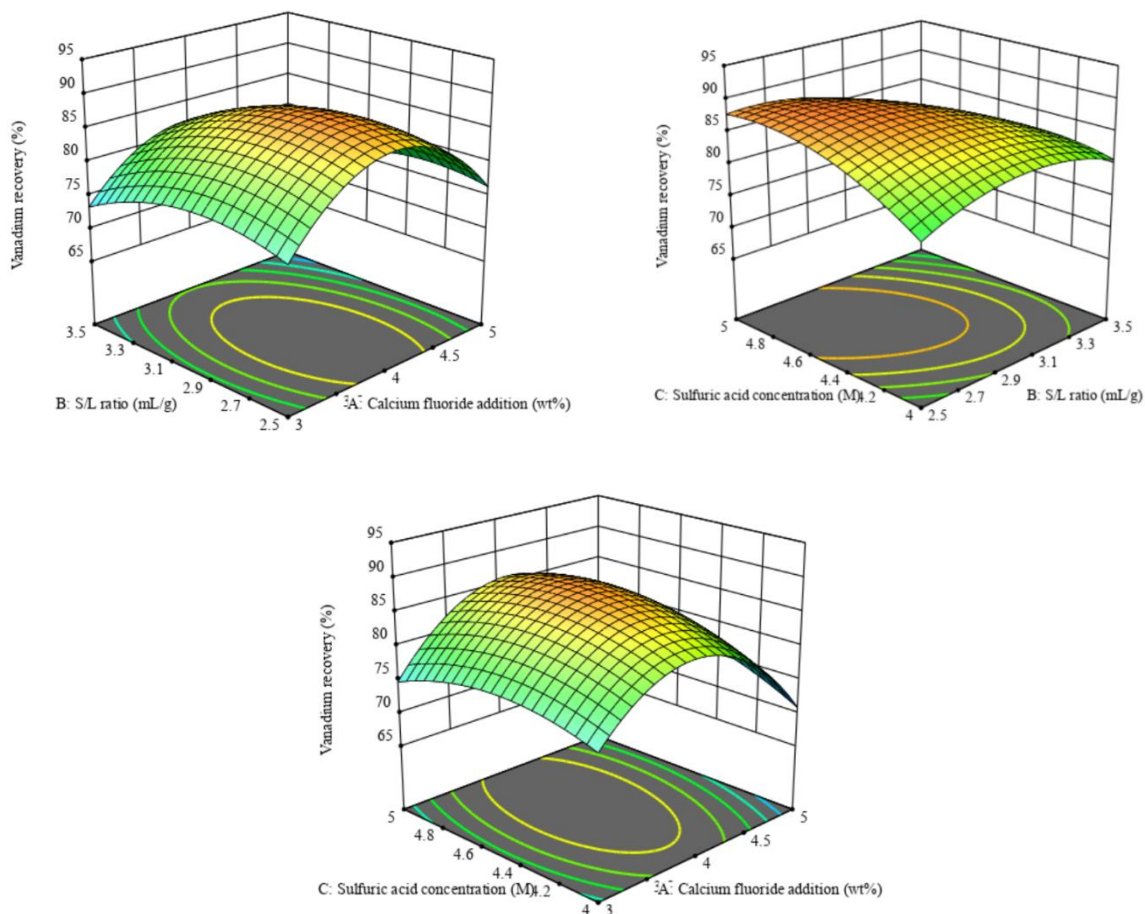
Fig. 2. Response 3D surface and contour plots of vanadium recovery versus: calcium fluoride addition and S/L ratio (left), S/L ratio and sulfuric acid concentration (right), and calcium fluoride addition and sulfuric acid concentration (bottom) (All surface graphs with respect to the center point configuration

3.2 Effect of calcium fluoride addition, S/L ratio, and sulfuric acid concentration on vanadium recovery

As shown in the results and in previous study of Zhu et al. (2016), the addition of calcium fluoride facilitates more efficient vanadium recovery by reducing the sulfuric acid consumption and improving the overall leaching efficiency [4]. However in Figure , there is a noticeable decrease in vanadium recovery after the addition of 4 % CaF_2. This is attributed to the generation of excess $CaSO_4$ during the leaching process. By Le Chatelier's principle, excess $CaSO_4$ will facilitate the reverse reaction shown in (3), impending the formation of hydrofluoric acid which in turn decreases vanadium recovery. Meanwhile, the interaction between S/L ratio and sulfuric acid concentration is shown in Figure 3 . It is observed that for a acid concentration greater than 4.6 M, vanadium recovery decreases. In vanadium leaching, high concentrations of sulfuric acid may cause reactions with silica present in the ore, which produces silica gel [11].The silica gel decreases vanadium recovery by adsorbing vanadium cations present in the solution such as in VO^{2+} and VO_2^+ [7].
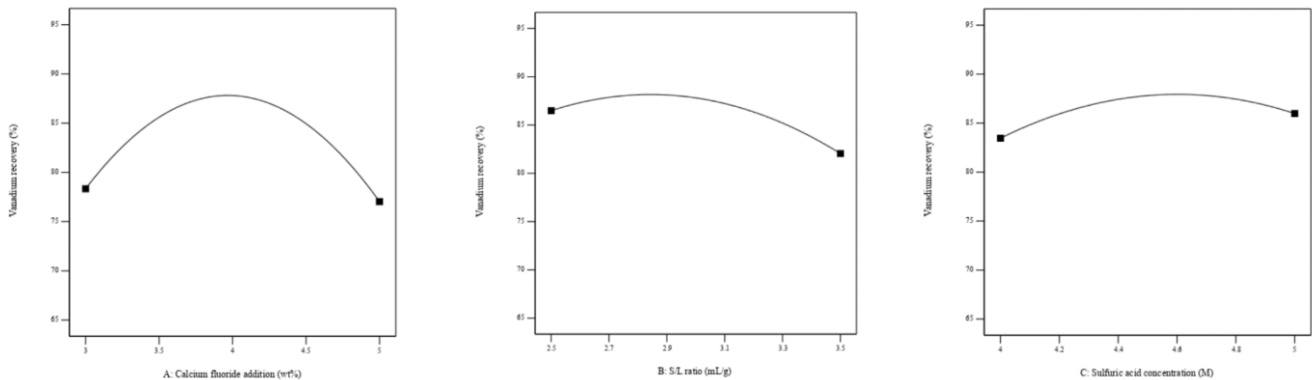

Fig. 3. Effect of calcium fluoride addition (left), solid-to-liquid ratio (center), and sulfuric acid concentration (right) to the vanadium recovery.

3.3 Process optimization using desirability functions

A multiple response method was used in order to any of the three factors: calcium fluoride addition, S/L ratio, and sulfuric acid concentration [7]. Based on the generated desirability graph in Figure 4 using multiple optimum points, the local maximum for vanadium recovery was found at 4.02 wt.% calcium fluoride, 2.74 mL/g ratio, and 4.73 M sulfuric acid concentration, which results in a vanadium recovery of 88.67%. This is close to the vanadium recovery obtained in the model, with a margin of 3.4%.
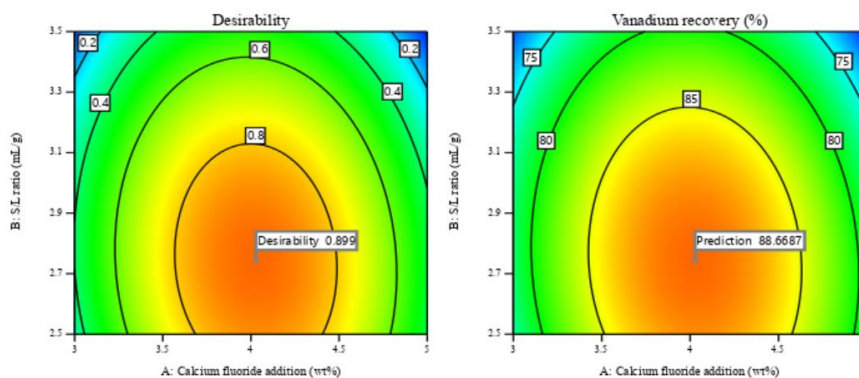

Fig. 4. Optimum conditions for vanadium recovery based on desirability functions

4. Conclusion

The study examined the feasibility of vanadium extraction from iron ores in the Philippines using direct leaching, a method that is considered to be more effective and environment-friendly than the conventional roasting-leaching route. Optimization of the direct leaching process was employed using Response surface methodology (RSM) based on Box-Behnken Design (BBD). The statistical analyses of the second-order polynomial model of the direct leaching method is a reliable response predictor of vanadium recovery, with a good correlation between the predicted and experimental values (R^2=0.9317). The optimum calcium fluoride addition, S/L ratio, and sulfuric acid concentration are , 4.02%, , 2.74 mL/g, and 4.73 M, respectively. Under these conditions, vanadium recovery of 88.67% is achieved. The results of the vanadium extraction via direct leaching showed promising results when compared to the conventional roasting-leaching route. This is an indication that vanadium extraction from iron ores in the Philippines is indeed feasible and can be applied to the industrial scale.

Acknowledgments

References

[1] Gilligan, Rorie & Nikoloski, Aleksandar. (2020). The extraction of vanadium from titanomagnetites and other sources. Minerals Engineering. 146. 10.1016/j.mineng.2019.106106.

[2] Vanadium. United States Geologic Survey.

[3] Li, Renmin & Liu, Tao & Zhang, Yimin & HUANG, JING & Xu, Chengbao. (2018). Efficient Extraction of Vanadium from Vanadium–Titanium Magnetite Concentrate by Potassium Salt Roasting Additives. Minerals. 8. 25. 10.3390/min8010025.

[4] Zhu, Xiaobo & Li, Wang & Guan, Xuemao. (2016). Vanadium extraction from titano-magnetite by hydrofluoric acid.

International Journal of Mineral Processing. 157. 10.1016/j.minpro.2016.09.01

[5] Fudolig et al. (2018). Ironmaking of magnetite sand concentrates using the rotary kiln-electric arc (RKEF) process. Philippine Metals. 5.

[6] Zhu, H., Fu, Y., Jiang, R., Yao, J., Xiao, L., Zeng, G., 2014. Optimization of copper (II) adsorption onto novel magnetic calcium alginate/maghemite hydrogel beads using response surface methodology. Industrial & Engineering Chemistry Research

53 (10), 4059–4066. https://doi.org/10.1021/ie4031677.

[7] Nejad, Davood & Taghizadeh, Majid & Khanchi, Ali. (2019). Vanadium extraction from magnetite ore using alkaline roasting and acid leaching processes: optimization of parameters by response surface methodology. 10. 241-255. 10.22044/jme.2018.7578.1610.

[8] Liu, Yi, Wang, Jintao, Zheng, Yian, Wang, Aiqin, 2012. Adsorption of methylene blue by kapok fiber treated by sodium chlorite optimized with response surface methodology. Chem. Eng. J. 184, 248–255.

[9] Zhu, H., Fu, Y., Jiang, R., Yao, J., Xiao, L., Zeng, G., 2014. Optimization of copper (II) adsorption onto novel magnetic calcium alginate/maghemite hydrogel beads using response surface methodology. Industrial & Engineering Chemistry Research 53 (10), 4059–4066. https://doi.org/10.1021/ie4031677.

[10] Perez, Jem Valerie D., Nadres, Enrico T., Nguyen, Hang Ngoc, Dalida, Maria,Lourdes P., Rodrigues, Debora F., 2017. Response surface methodology as a powerful tool to optimize the synthesis of polymer-based graphene oxide nanocomposites for simultaneous removal of cationic and anionic heavy metal contaminants. Royal Society of Chemistry Advances 7 (30), 18480–18490. https://doi.org/10.1039/C7RA00750G.

[11] LIU, Bing-guo & PENG, Jin-hui & WAN, Run-dong & ZHANG, Li-bo & GUO, Sheng-hui & ZHANG, Shi-ming. (2011). Optimization of preparing V2O5 by calcination from ammonium metavanadate using response surface methodology[J]. Transactions of Nonferrous Metals Society of China - TRANS NONFERROUS METAL SOC CH. 21. 673-678. 10.1016/S1003-6326(11)60764-4.

[12] Pan, Bo & Liu, Biao & Wang, Shaona & Wenzel, Marco & Weigand, Jan & Feng, Man & Du, Hao & Zhang, yi. (2020). Ammonium vanadate/ammonia precipitation for vanadium production from a high vanadate to sodium ratio solution obtained via membrane electrolysis method. Journal of Cleaner Production. 263. 121357. 10.1016/j.jclepro.2020.121357.